Emerging and historical halogenated flame retardants in fish samples from Iberian rivers: BSAF estimation.

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Introduction

FLAME RETARDANTS (FRs)

- Chemicals added to polymeric materials, both natural and synthetic, such as plastics, wood, paper, and textiles, to enhance flame-retardance properties.

- Global annual demand increases every year (expected to rise by 6.1% per year, reaching 2.2 million mt by 2014).

- The four major groups are inorganic, halogenated organic, organophosphorus and nitrogen-based flame retardants (in order of the annual production)

*Polybrominated diphenyl ethers (PBDEs)*

- 209 Congeners

- High lipophilicity

- They bioaccumulate and biomagnified along the food chain.

- Toxic for the environment and human being.

Introduction

**Emerging Brominated FRs**

- Pentabromoethylbenzene (PBE)
- Hexabromobenzene (HBB)
- Decabromodiphenylethane (DBDPE)

**Halogenated Norbornenes Flame Retardants**

- Dechlorane Plus (DP)
- Dechlorane 602 (Dec 602)
- Dechlorane 603 (Dec 603)
- Dechlorane 604 (Dec 604)
Sampling

Guadalquivir (n=4)

Ebro (n=16)

Llobregat (n=11)

Júcar (n=17)
Experimental

Sample Treatment

3 g (dw) fish

Spiked overnight with 5 ng BDE-181 and 50 ng $^{13}$C-BDE-209

PLE

$T^\circ$: 100 ºC
Pressure: 1500 psi
Solvent: Hexane:DCM (1:1)

Fat content determination

H$_2$SO$_4$ Treatment

Solid Phase Extraction (SPE)

Incipient dryness

Final Volume: 40 µL

Instrumental Determination

PBDEs and Emergins BFRs

- GC Agilent Technologies 7890/MS Agilent Technologies 5975
- Column: DB-5MS (15 m x 0.25 mm x 0.1 µm film thickness)
- Carrier Gas: He
- Negative Chemical Ionization (CH$_4^+$)
- Program: 140 ºC hold for 2 min, 10 ºC/min to 325 ºC, hold 10 min.
- Total run time: 30.5 min

Dechloranes

- GC Agilent Technologies 7890/MS-MS Agilent Technologies 7000
- Column: DB-5MS (15 m x 0.25 mm x 0.1 µm film thickness)
- Carrier Gas: He
- Negative Chemical Ionization (NH$_3^+$)
- Program: 140 ºC hold for 2 min, 10 ºC/min to 300 ºC, hold 10 min.
- Total run time: 32 min

Spiked overnight with 5 ng BDE-181 and 50 ng $^{13}$C-BDE-209
Results: PBDEs and Emerging BFRs

**PBDEs**
- All PBDEs were detected, with the exception of BDE-99.
- The most abundant congener was BDE-47, followed by BDE-100, BDE-153~BDE-154, BDE-183, BDE-28 and BDE-209.
- Total PBDE concentrations were in a range of BDL-520 ng/g lw.
- The contamination level order between the four river basins was:
  - Llobregat (55.9-520 ng/g lw) > Ebro (BDL-90.9 ng/g lw) > Júcar (BQL-69.3 ng/g lw) > Guadalquivir (BDL-7.94 ng/g lw)

**Emerging BFRs**
- Only DBDPE was found in the samples.
- The concentrations were in a range of BDL-130 ng/g lw.
- The contamination level order between the four river basins was:
  - Llobregat (55.9-130 ng/g lw) > Ebro (BDL-21.6 ng/g lw) ~ Júcar (BQL-20.0 ng/g lw) > Guadalquivir (BDL-BQL ng/g lw)
Results: PBDEs and Emerging BFRs

PBDEs Boxplot

DBDPE Boxplot
Results: PBDEs and Emerging BFRs

**Ebro**

- ng/g lw
- OCA, EBR2, EBR3, EBR4, EBR5
- Barbus Graelissi (Juvenile)
- Barbus Graelissi (Adult)
- Cyprinus Carpio

**Ebro DBDPE**

- ng/g lw
- OCA, EBR2, EBR3, EBR4, EBR5
- Barbus Graelissi (Juvenile)
- Barbus Graelissi (Adult)
- Cyprinus Carpio

**Llobregat**

- ng/g lw
- LLO3, LLO4, LLO5, LLO6, LLO7
- Barbus Graelissi (Juvenile)
- Barbus Graelissi (Adult)
- Cyprinus Carpio

**Llobregat DBDPE**

- ng/g lw
- LLO3, LLO4, LLO5, LLO6, LLO7
- Barbus Graelissi (Juvenile)
- Barbus Graelissi (Adult)
- Cyprinus Carpio
Results: Dechlororanes

- Dec-602 > Dec-603 > syn-DP > anti-DP
- Dec-604 was not found in any sample
Results: $f_{\text{anti}}$

$$f_{\text{anti}} = \frac{\text{Concentration } anti-\text{DP}}{\text{Concentration } syn-\text{DP} + anti-\text{DP}}$$

Commercial Mixture

0.67-0.75
Results: BSAF estimation

BSAF = \frac{\text{Contaminant Concentration in Fish (ng/g lw)}}{\text{Contaminant Concentration in Sediment (ng/g ow)}}

These results were made with the Ebro and Llobregat river data.

- PBDE BSAFs gets lower when the number of bromine in the molecule increases.

<table>
<thead>
<tr>
<th></th>
<th>LLO4</th>
<th>LLO6</th>
<th>LLO3</th>
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<tbody>
<tr>
<td>Penta-BDE</td>
<td>4.43</td>
<td>22.1</td>
<td>17.3</td>
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<tr>
<td>Hexa-BDE</td>
<td>2.42</td>
<td>5.09</td>
<td>0.14</td>
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</table>

- DBDPE BSAF is similar to BDE-209.

<table>
<thead>
<tr>
<th></th>
<th>LLO4</th>
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<tbody>
<tr>
<td>BDE-209</td>
<td>0.02</td>
</tr>
<tr>
<td>DBDPE</td>
<td>0.03</td>
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</table>
• HFR BSAFs are lower than the PBDEs
• BSAF order for Dechloranes was Dec-602>Dec-603>DP.
• BSAFs for syn-DP are higher than those for anti-DP.

<table>
<thead>
<tr>
<th></th>
<th>OCA</th>
<th>EBR2</th>
<th>EBR3</th>
<th>EBR4</th>
<th>LLO5</th>
<th>LLO7</th>
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<tbody>
<tr>
<td></td>
<td>Barbel (Adult)</td>
<td>Barbel (Juvenile)</td>
<td>Barbel (Adult)</td>
<td>Barbel (Juvenile)</td>
<td>Barbel (Adult)</td>
<td>Barbel (Juvenile)</td>
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<tr>
<td>BDE-100</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
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<tr>
<td>BDE-154</td>
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<td>BDE-153</td>
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<tr>
<td>Dec-602</td>
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<td>-</td>
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<tr>
<td>Dec-603</td>
<td>15,17</td>
<td>0,49</td>
<td>4,46</td>
<td>0,69</td>
<td>0,26</td>
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<tr>
<td>syn-DP</td>
<td>0,11</td>
<td>1,08</td>
<td>0,32</td>
<td>1,18</td>
<td>0,14</td>
<td>0,09</td>
</tr>
<tr>
<td>anti-DP</td>
<td>0,03</td>
<td>0,37</td>
<td>0,29</td>
<td>0,49</td>
<td>0,04</td>
<td>0,03</td>
</tr>
</tbody>
</table>

• Barbel BSAF > Common Carp BSAF.
Conclusions

• PBDEs, Emerging BFRs and Dechloranes were detected in fish samples collected along four Iberian river basins.

• Llobregat is the most contaminated river basin followed by Ebro, Júcar and Guadalquivir in almost every analyzed contaminant.

• $f_{\text{anti}}$ values in sediments are similar to those of technical product, whereas $f_{\text{anti}}$ values decreased in biota samples. This behavior could be explained by a higher bioaccumulative potential of syn-DP versus anti-DP.

• BSAF were estimated, and values for Dechloranes were lower than those of PBDEs.
Thank you for your attention

In memory of the fish that died during the process of sampling